

Towards Bonding Structure and Dynamics in Molecular Systems

A Study of Water from Ambient to Supercritical Conditions With X-ray Spectroscopy

Philippe Wernet

BESSY

Acknowledgements and Collaborations

„Water Collaborations“

Anders Nilsson and group	SSRL
Uwe Bergmann	SSRL
Lars Pettersson and group	Stockholm University
Jean-Louis Hazemann and group	CNRS, Grenoble

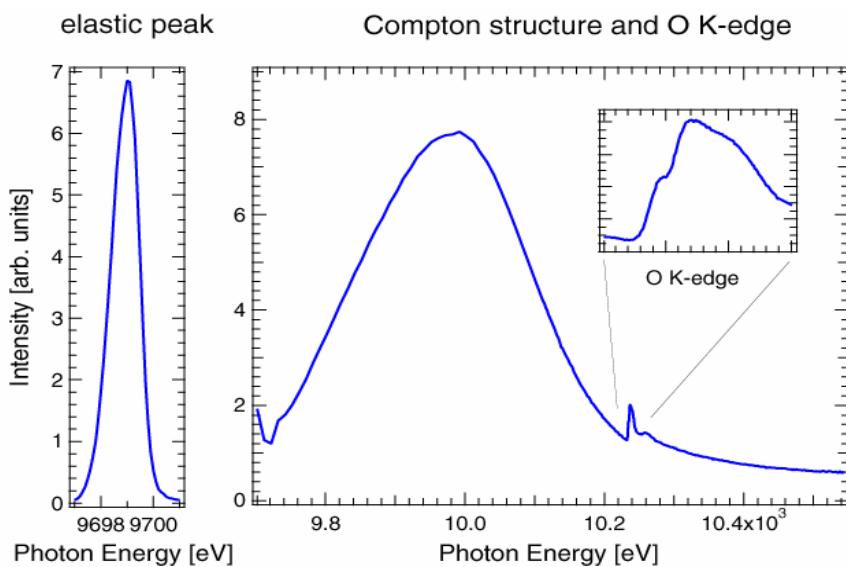
@ BESSY

HHG - dynamics	static solution expts.
Kai Godehusen	Emad Aziz
Olaf Schwarzkopf	Stefan Eisebitt
Wolfgang Eberhardt	
+ „Laser crew“	

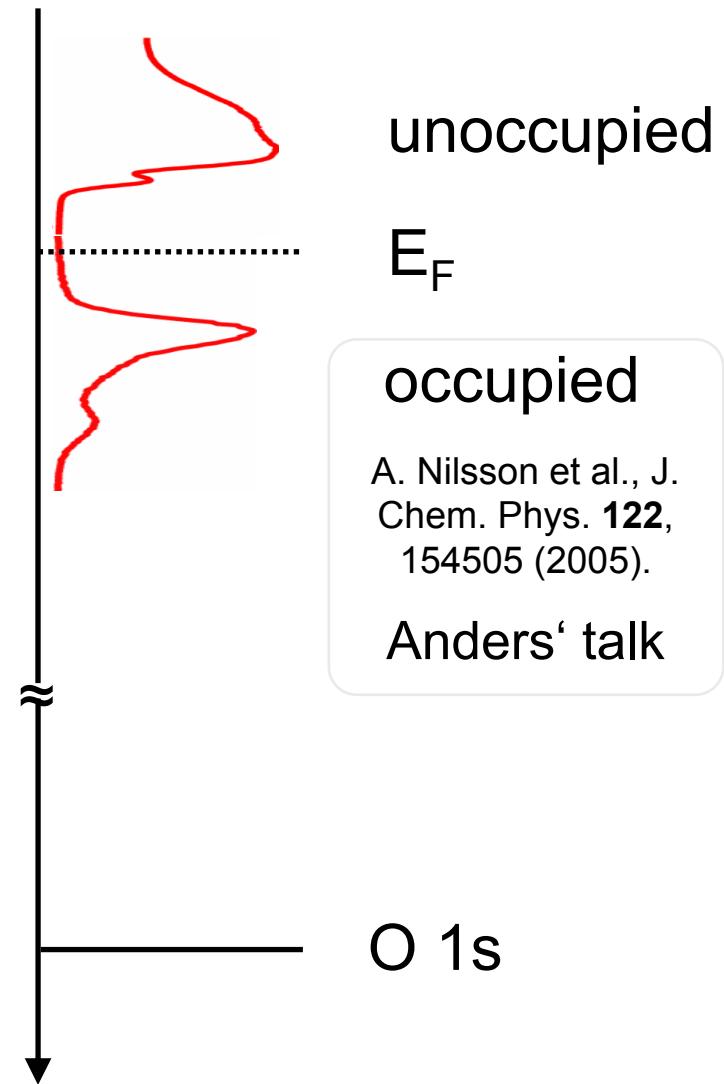
„Why (Soft) X-rays?“

binding energy

„Hard x-ray in – soft x-ray edge out“



Bergmann, Wernet, Glatzel et al., PRB **66**,
092107 (2002).



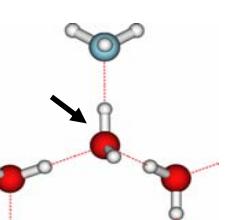
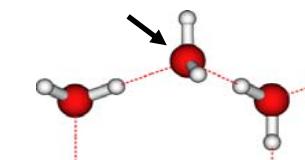
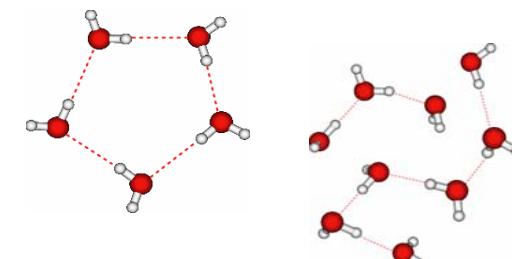
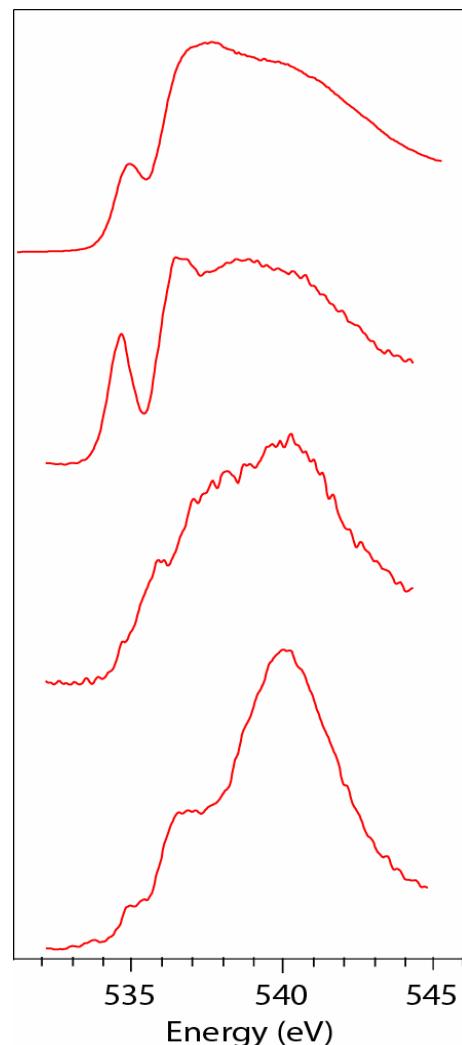
Water: Bonding and Structure

liquid water

ice surface

NH₃ covered
ice surface

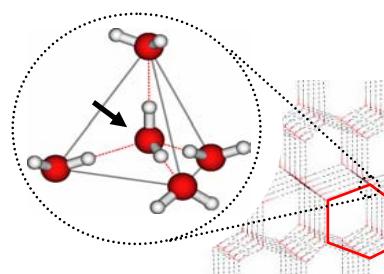
bulk ice



broken bonds

D. Nordlund et al.,
CPL 395, 161
(2004).

saturated bonds



tetrahedral
coordination
4 bonds per
molecule

80% (15%) of molecules in liquid with 1 strong donor H-bond (4-coordinated)

Experiment

Theory

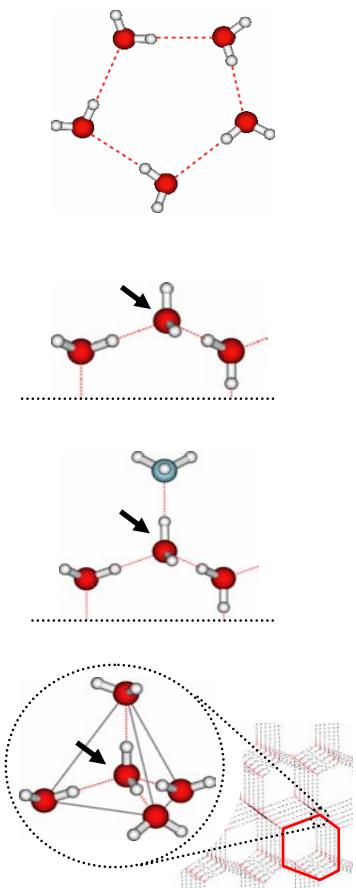
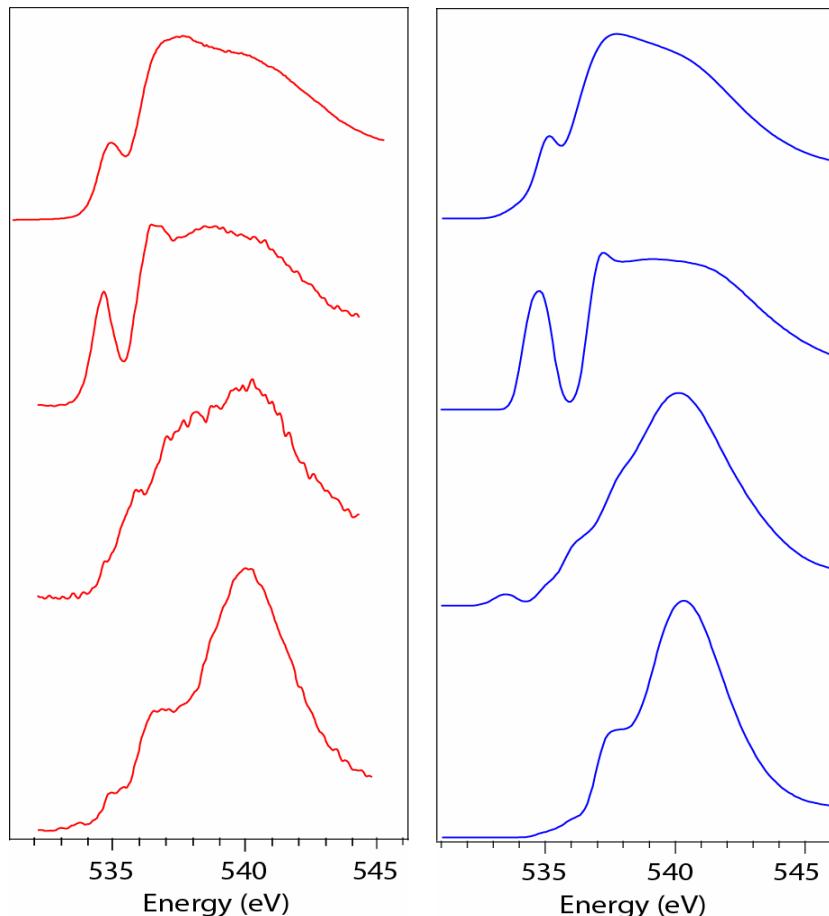
Water Structure

liquid water

ice surface

NH₃ covered
ice surface

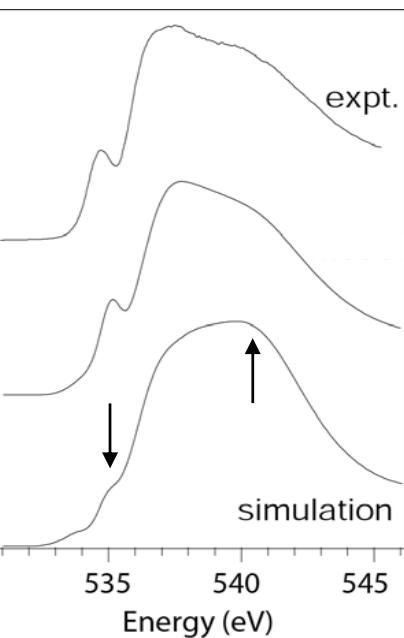
bulk ice



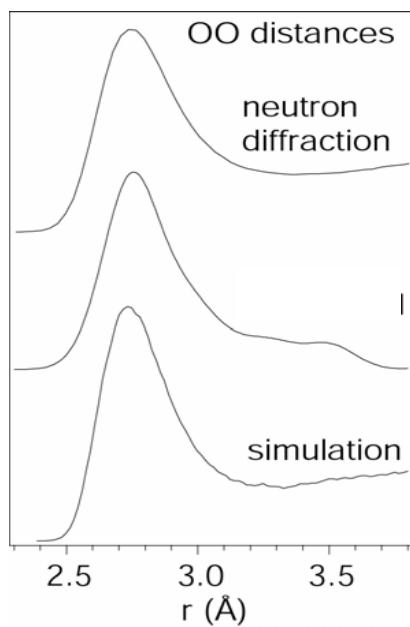
- 80% (15%) of molecules in liquid with 1 strong donor H-bond (4-coordinated)
- **Asymmetric model: 2 H-bonds per molecule in liquid water (rings, chains)**

Liquid Water Structure Revisited

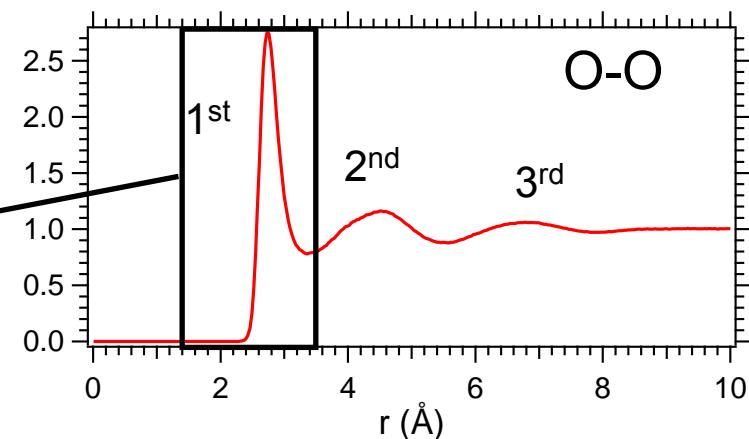
x-ray absorption



O-O distances



nearest neighbor O-O distances



Asymmetric model

Most molecules in liquid water with 2 H-bonds
1 donor / 1 acceptor

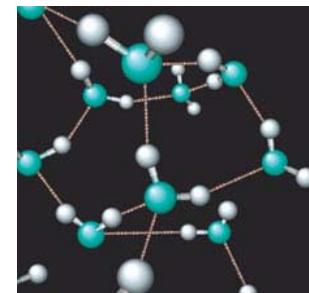
Wernet et al., Science **304**, 995 (2004)

Against the current belief (not against experimental results)

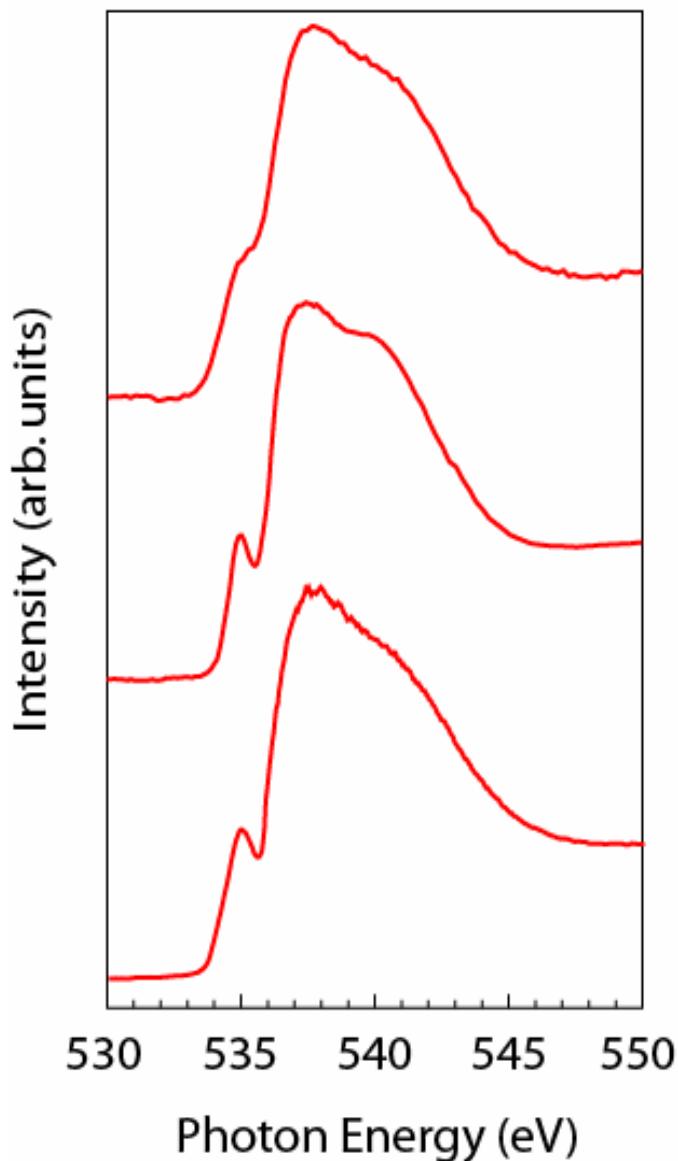
“Infinite network of disordered tetrahedral water.”

MD simulations!

~3.5 H-bond / molecule



XAS + XRS of Liquid Water

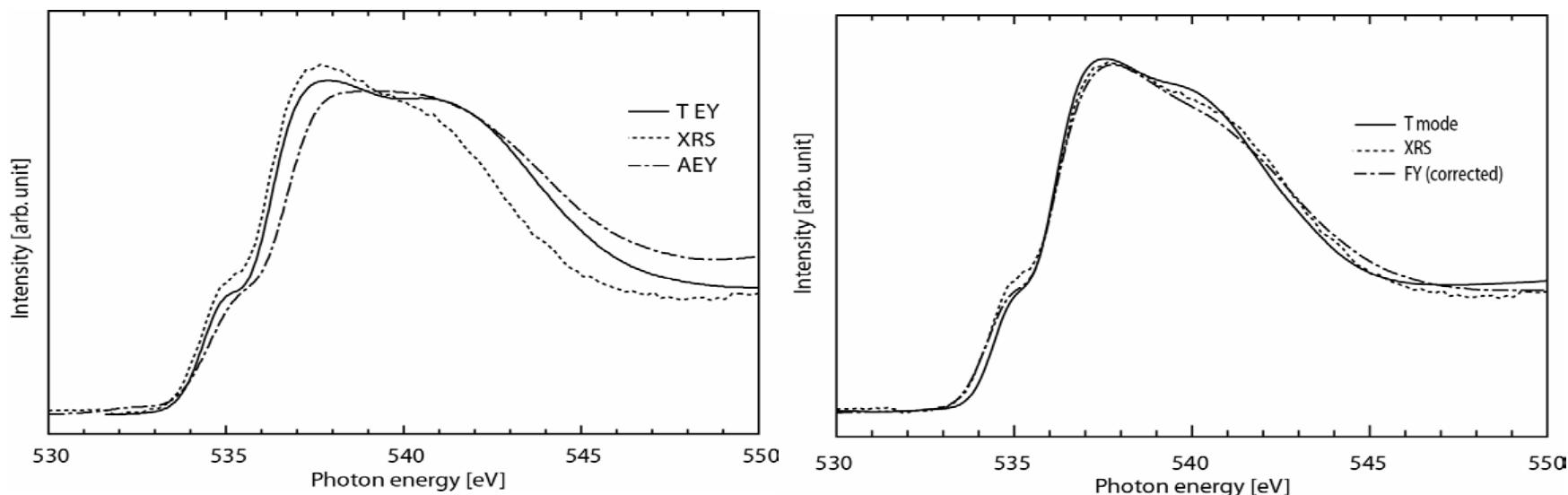


hard x-ray
Raman
scattering

transmission

fluorescence
yield (corrected)

Comparison of Different Methods



XRS (T-XAS) only reliable way to measure small changes

AEY: Salmeron et al.

TEY: Saykally et al.

L. A. Näslund et al., J. Phys. Chem.
B 109, 13835 (2005)

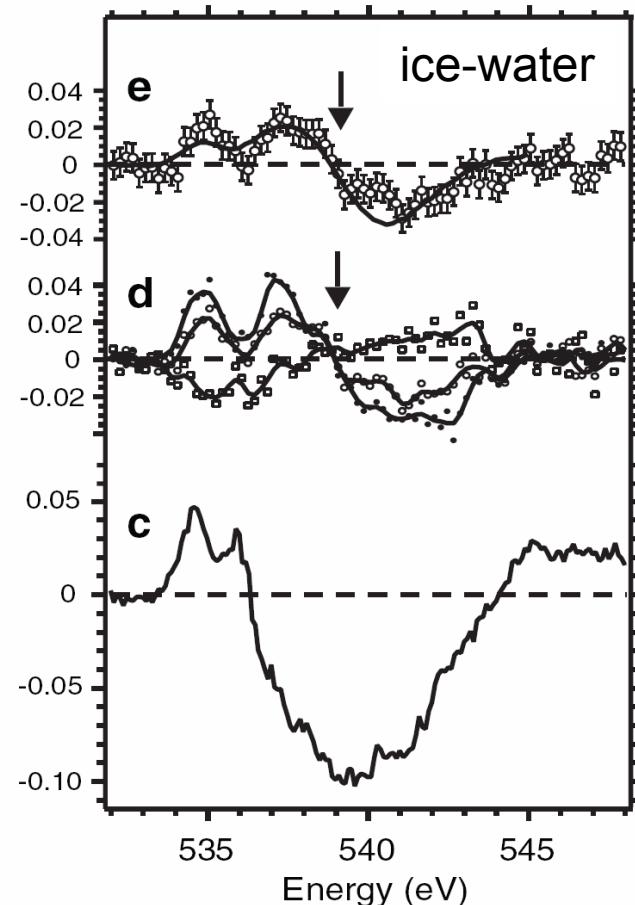
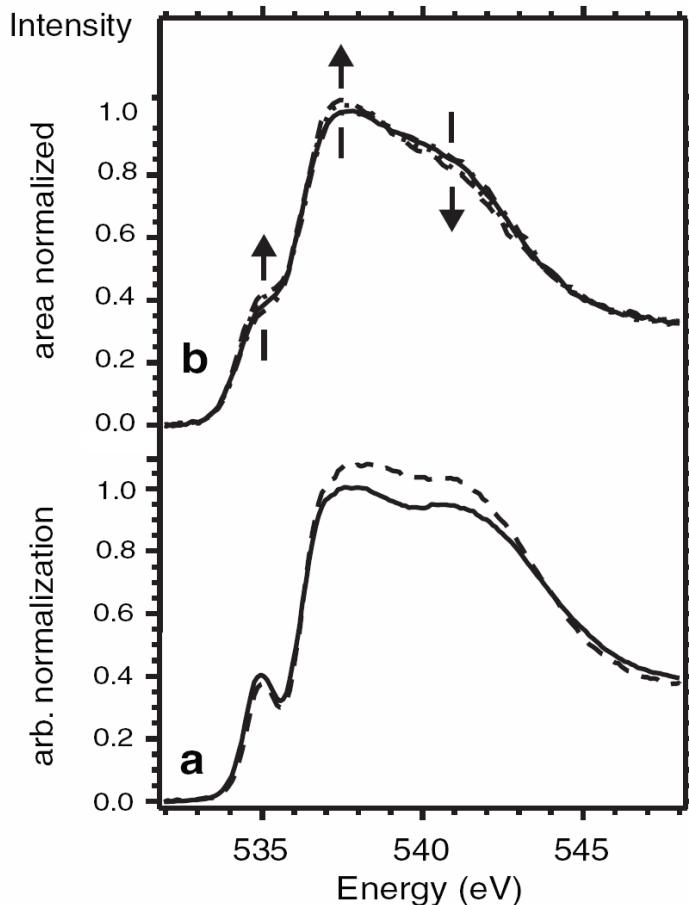
Temperature Dependence

XRS

3.5, 25, 59, 90 °C
(A. Nilsson et al.)

electron yield

-19, 15 °C
(Smith et al.)



XRS highly sensitive + accurate (reproducible)

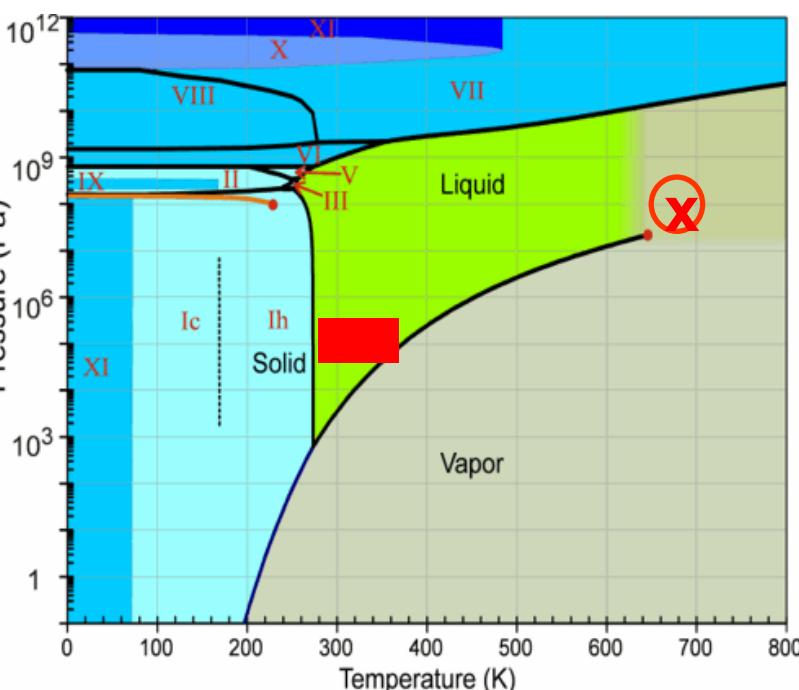
Vernet et al., Science **304**, 995 (2004).

J. Smith et al., Science **306**, 851 (2004).

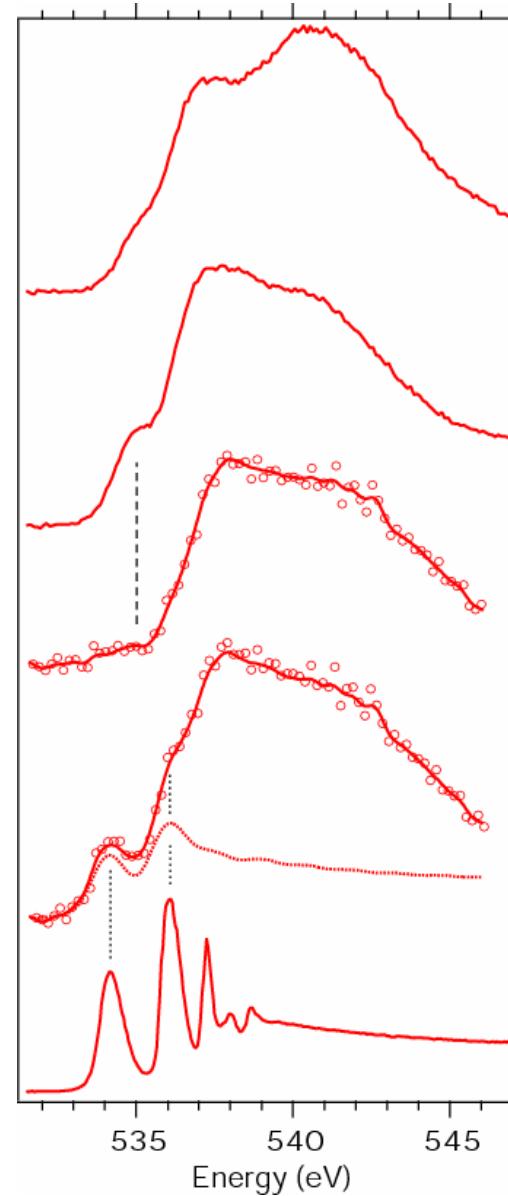
A. Nilsson, et al. Science **308**, 793a (2005).

J. Smith et al., Science **308**, 793b (2005).

Supercritical Water



XRS
380 °C
300 bar
0.5 g/cm³



Ice

Liquid water

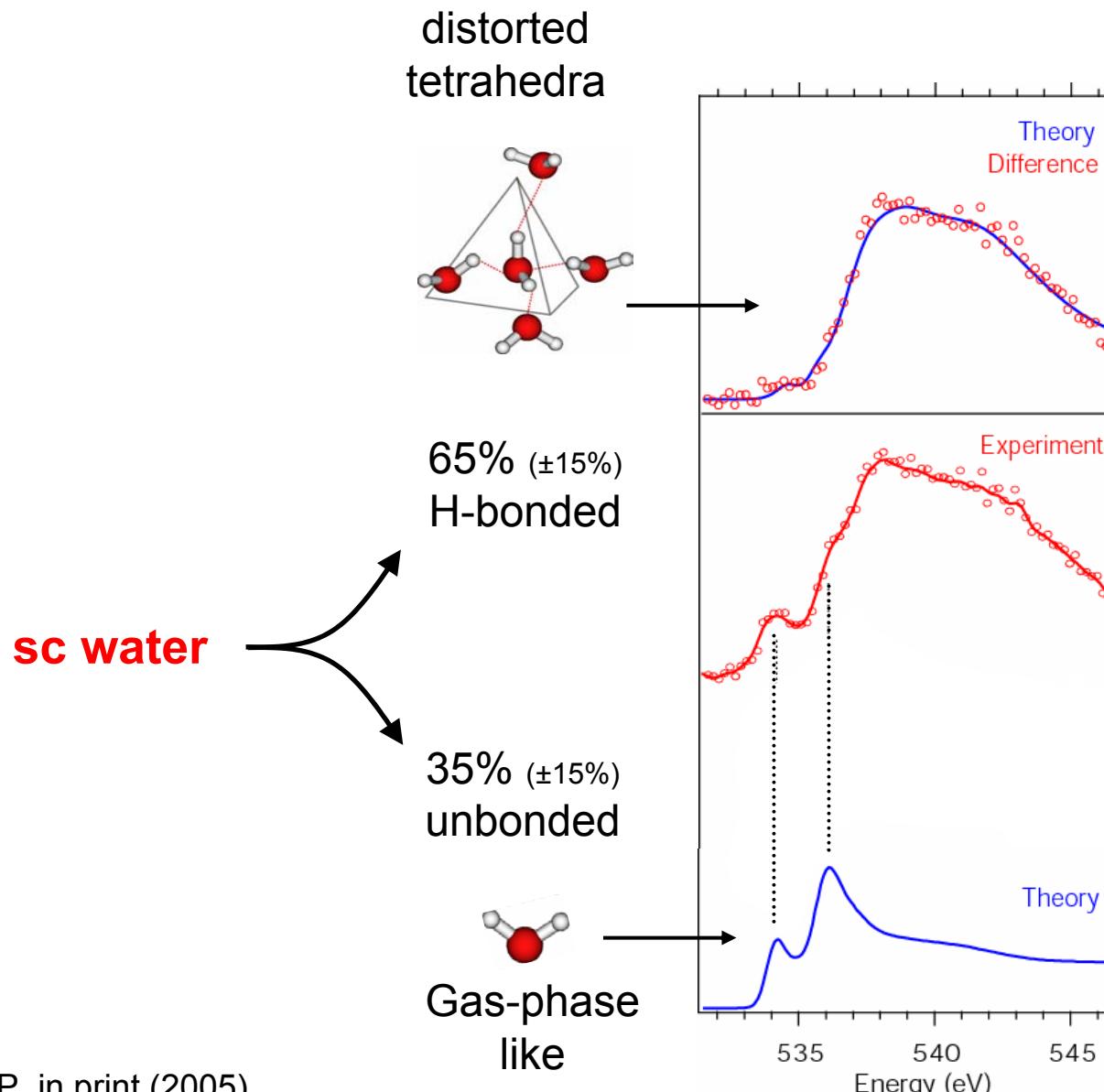
Difference
SC water – 35% vapor

SC water

35% water vapor
(convoluted)

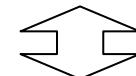
Water vapor
(absorption)

Disparate H-bonding Configurations



- In the gas phase
- In solution

Intramolecular bonds

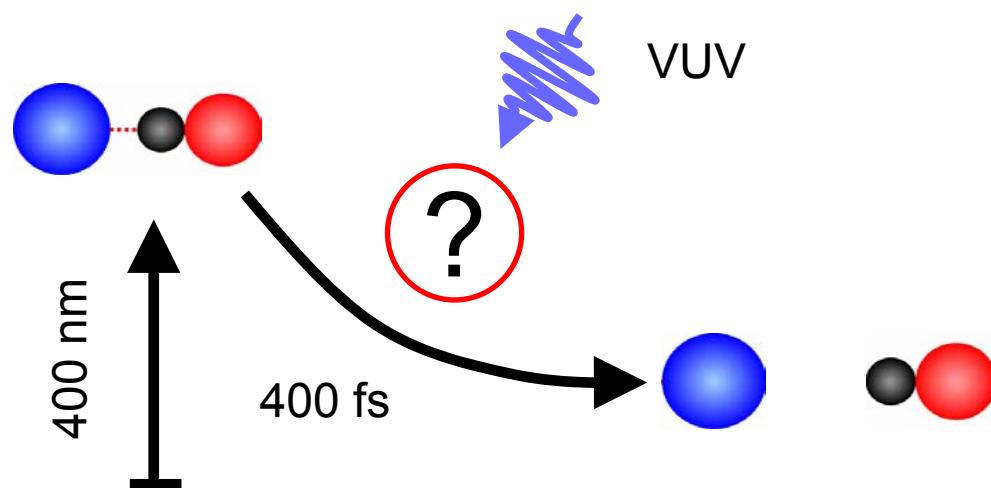


Intermolecular bonds

With soft x-ray spectroscopy: XAS, XES, UPS, XPS...

→ synchrotron (ps, 200-1000 eV), „slicing“ (fs, 200-1000 eV), **HHG (fs, 20 eV)**

→ **Spectroscopy at soft x-ray Free Electron Lasers (FEL)**



Electronic structure in
real time:

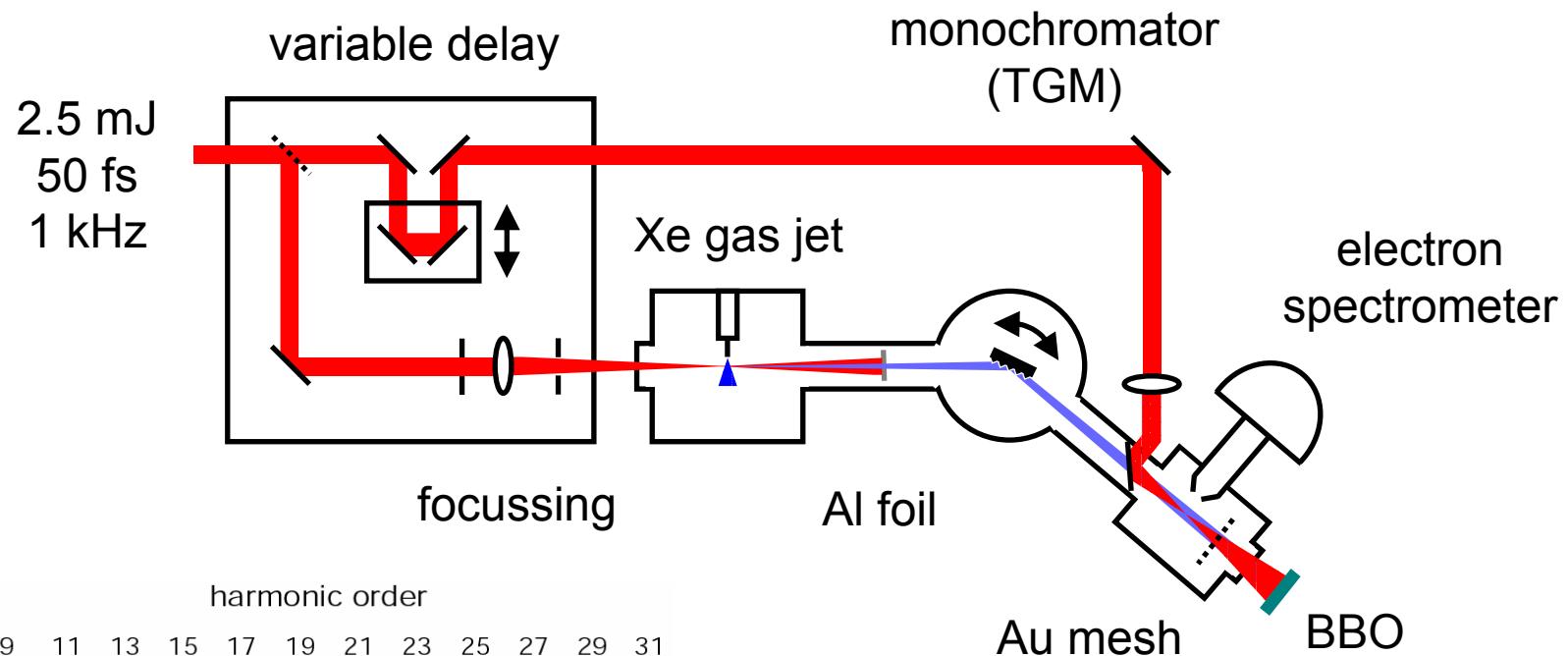
„x-ray femtochemistry“

IR / visible pump

–

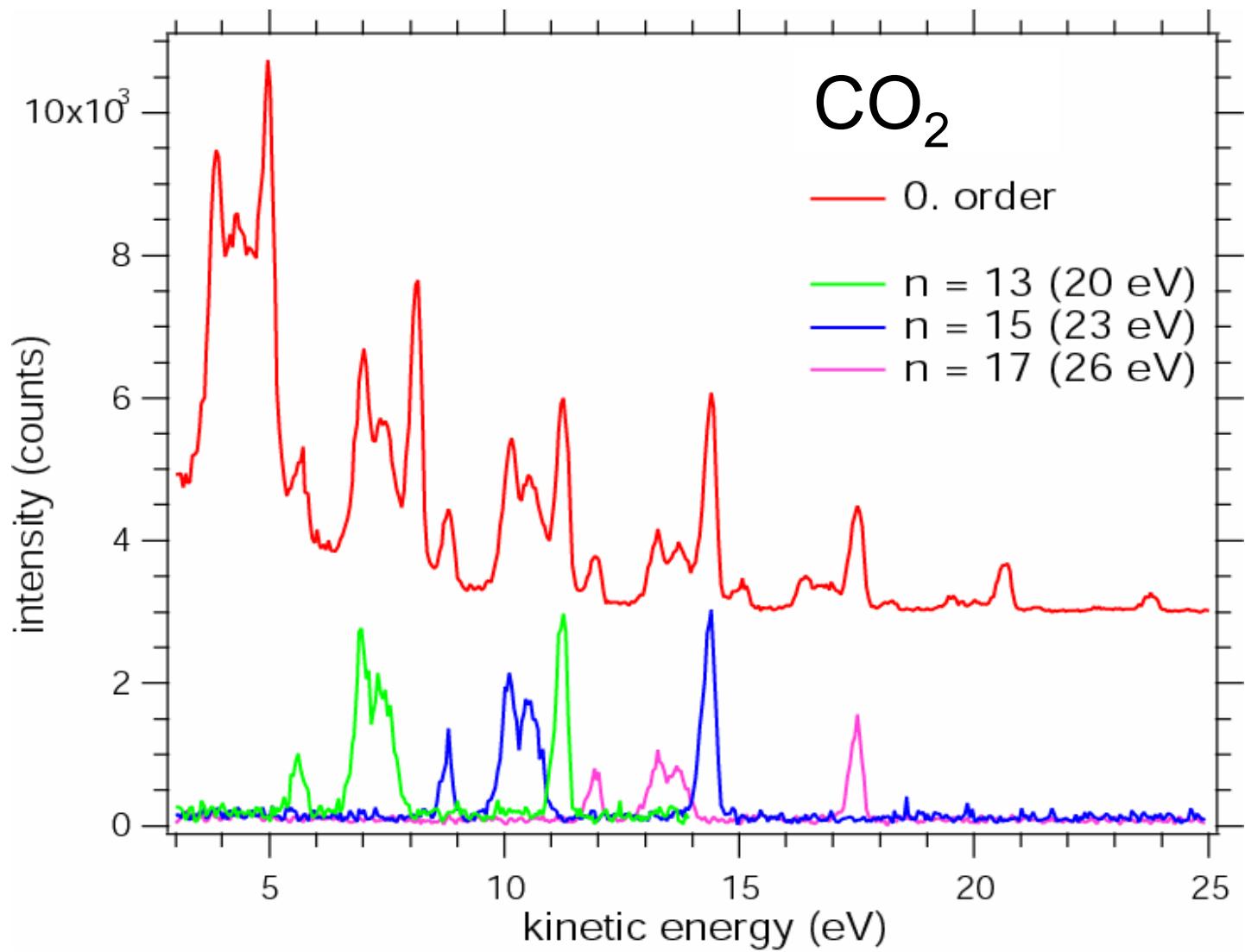
VUV / x-ray probe

High Harmonic Generation: Setup and flux curve



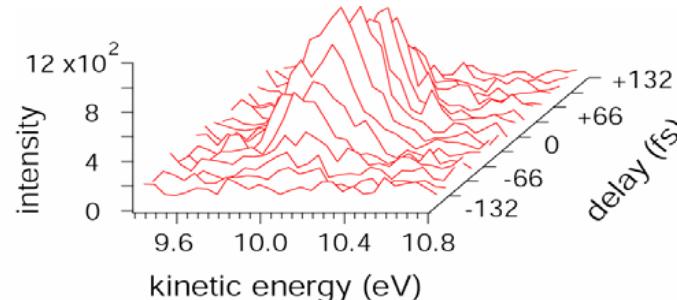
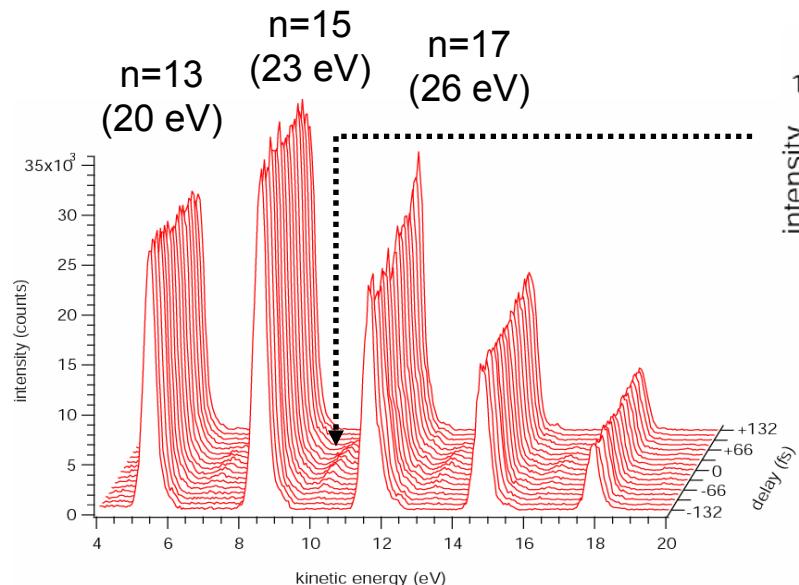
$10^9 - 10^{10}$ photons / s
 at sample, 20-30 eV, ~1 mm spot size in 0.25 eV bandwidth, <1mrad divergence)
 10^4-10^5 times more photons / pulse compared to synchrotron

VUV Photoelectron Spectroscopy in the gas phase



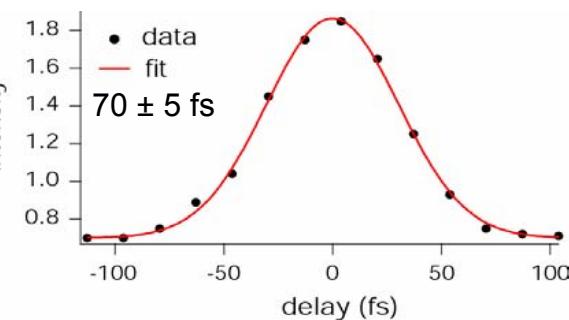
IR-VUV cross correlation

Ar 3p
photoelectron
spectra
(monochromator
in zero order)

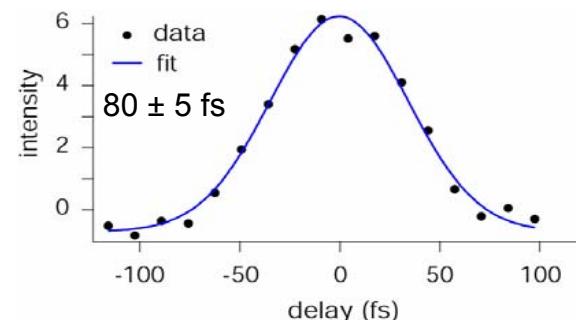


sideband intensity as a
measure of temporal
overlap

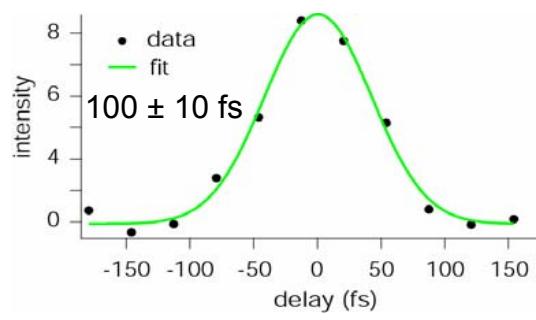
IR-IR



IR-VUV (0. order)



IR-VUV (1. order)



50 fs IR



60 fs VUV



90 fs VUV

pulse broadening by grating <100 fs

- Why x-rays?
 - Address specialized communities outside x-rays
 - Theory (soft x-ray spectroscopy)
-
- Liquids (Water, dilute systems)
 - Solute-solvent interactions, H-bonding
 - Dynamics (IR / visible pump - x-ray probe)
 - Ultrafast chemical reaction dynamics

Bonding, Structure and Dynamics in Molecular systems